

# EXPERIMENTAL CONSTRAINTS ON THE STABILITY OF CLINOPYROXENE + MAGNESITE IN IRON BEARING PLANETARY MANTLES: IMPLICATIONS FOR NAKHLITE FORMATION.

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**Introduction:** Carbon is present in various forms in the Earth's upper mantle (carbonate- or diamond-bearing mantle xenoliths, carbonatite magmas, CO<sub>2</sub> emissions from volcanoes...). Moreover, there is enough carbon in chondritic material to stabilize carbonates into the mantles of Mars or Venus as well as in the Earth. However, the interactions with iron have to be constrained, because Fe is commonly thought to buffer oxygen fugacity into planetary mantles. [1] and [2] show evidences of the stability of clinopyroxene Ca(Mg,Fe)Si<sub>2</sub>O<sub>6</sub> + magnesite (Mg,Fe)CO<sub>3</sub> in the Earth's mantle around 6GPa (about 180km). The stability of oxidized forms of carbon (like magnesite) depends on the oxygen fugacity of the system. In the Earth's mantle, the maximum carbon content is 10000 ppm [3]. The fO<sub>2</sub> parameter varies vertically as a function of pressure, but also laterally because of geodynamic processes like subduction. Thus, carbonates, graphite, diamond, C-rich gases and melts are all stable forms of carbon in the Earth's mantle. [4] show that the fO<sub>2</sub> variations observed in SNC meteorites can be explained by polybaric graphite-CO-CO<sub>2</sub> equilibria in the Martian mantle. [5] inferred from thermodynamic calculations that the stable form of carbon in the source regions of the Martian basalts should be graphite (and/or diamond). After [6], a metasomatizing agent like a CO<sub>2</sub>-rich melt may infiltrate the mantle source of nakhlites. However, according to [7] and [8], the FeO wt% value in the Martian bulk mantle is more than twice that of the Earth's mantle (KLB-1 composition by [9]). As iron and carbon are two elements with various oxidation states, Fe/C interaction mechanisms must be considered.

**Experimental Method:** The starting mixture was prepared using 50 mol% of natural magnesite (MgCO<sub>3</sub>) and 50 mol% of synthetic diopside glass (CaMgSi<sub>2</sub>O<sub>6</sub>). Fe/C ratios – and therefore, redox conditions – were changed by various methods: (1) replacing magnesite by natural siderite (FeCO<sub>3</sub>), (2) adding Fe metal powder to the system (two iron contents were tested, Table 1) and (3) using an internal graphite capsule. Experiments were performed in a piston-cylinder apparatus at 1.8 GPa – 1100 °C (Martian mantle temperature), 1200 °C and 1300 °C (Earth's mantle temperature). fO<sub>2</sub> in the samples is not known, but for experiments using graphite capsule and containing FeO bearing melts, FMQ-2 to FMQ-3 is expected [10].

**Results: Phase relations.** The assemblage clinopyroxene + magnesite is destabilized to form olivine (ol), clinopyroxene (cpx), calcite (cc), iron-oxides (Fe-ox), graphite (Gr) and melt in various proportions (Fig.1, Table 1). Three experiments were run above the liquidus. The fraction of melts is higher in the samples of the DS series of experiments than in the DM series. At 1300 °C, liquidus is passed only in the DS series. On contrary, the presence of iron metal makes the melt disappear in the two series of experiments at 1100 °C.

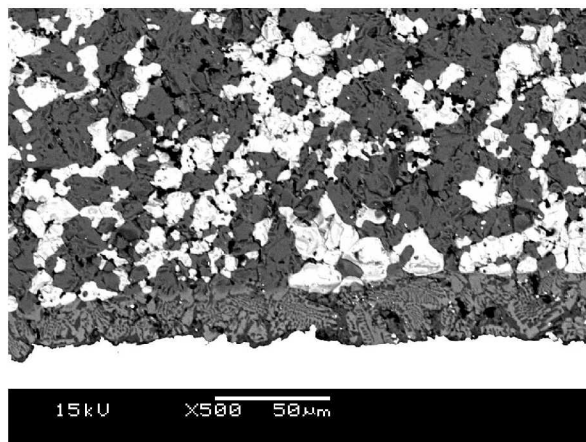


Fig.1: BSE image of a sample above the solidus temperature (DM series + 68 at% Fe at 1200 °C). The melt (at the bottom) contains about 15 wt% SiO<sub>2</sub> and 27 wt% CO<sub>2</sub>. Olivine (dark grey) and magnetite (white) are also present.

Table 1: Phase relations in the DM (diopside+magnesite) and DS (diopside+magnesite) series of experiments. The presence of graphite or CO<sub>2</sub> in the samples is not indicated.

T (C)	DM	DM+Graph	DM+Fe <sub>68</sub>	DM+Fe <sub>32</sub>
1100	Cpx+Ol +Melt	Cpx+Ol +Melt	Cpx+Ol +Fe-Ox+Cc	Cpx+Ol +Fe-Ox+Cc
1200	Cpx+Ol +Melt	Cpx+Ol +Melt	Ol+Fe-ox +Melt	Ol+Cpx+ Melt
1300	Cpx+Ol +Melt	Cpx+Ol +Melt	Ol+Fe-ox +Melt	Ol+Cpx+ Melt
T (C)	DS	DS+Graph	DS+Fe <sub>68</sub>	DS+Fe <sub>32</sub>
1100	Cpx+Ol +Melt	Cpx+Ol +Fe-ox+Melt	Cpx+Ol +Fe-ox	Cpx+Ol +Cc
1200	Cpx+Ol +Fe- ox+Melt	Cpx+Ol +Melt	Ol+Fe-Ox +Melt	Ol+Fe-ox +Melt
1300	Melt	Cpx+Ol +Melt	Melt	Melt

**Phase compositions and iron repartition.** Melts form a continuous trend in the  $\text{SiO}_2 - \text{CO}_2$  space which is very close to all the experimental data acquired on a peridotite/eclogite +  $\text{CO}_2$  system (Fig.2).

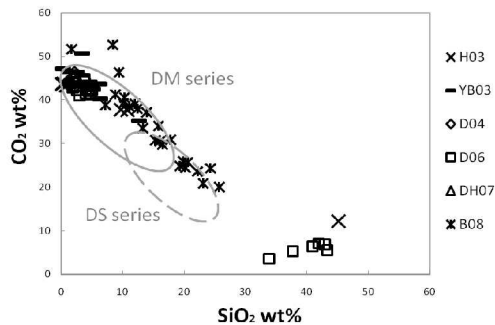


Fig.2: variations of  $\text{CO}_2$  vs.  $\text{SiO}_2$  in the melts, compared to the melts obtained in the eclogite +  $\text{CO}_2$  (H03[10], YB03[11], D04[12] and D06[13]) or peridotite +  $\text{CO}_2$  (DH07[14] and B08[15]) systems.

CaO content in the melts vary from 15 to 55wt%. FeO content in the melt is higher if the iron was added as siderite rather than Fe metal: between 10 and 50 wt% in the DS (diopside+siderite) series of experiments, but between 0 and 22 wt% in the DM (diopside+magnesite) experiments. FeO content in olivine and clinopyroxene is also higher in the DS series of experiments than in the DM series. Fe/Mg in the phases decreases as following: magnetite > melt > olivine > cpx (Fig.3). Adding iron – in the form of  $\text{Fe}^{2+}$  or Fe – to the starting material lowers the calcium content of the melts. This may be linked to an immiscibility between calcite and siderite [16]. The presence of iron also lowers the calcium content in clinopyroxene. On contrary, the Ca content in olivine is higher in the experiments with iron, which is coherent with the data obtained by [17] on a ferroan basalt.

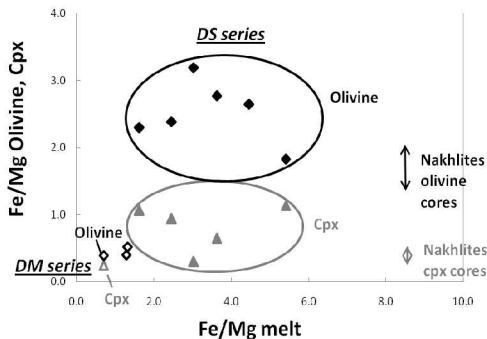


Fig. 3: Fe/Mg (at%) in olivine and cpx vs. Fe/Mg in the melt, compared to nakhlites olivine and cpx [18].

**Discussion: Role of Fe/C and  $f\text{O}_2$  on cpx+magnesite stability.** We show that the assemblage diopside + magnesite is not stable at 1.8 GPa between 1100 and 1300 °C. The presence of  $\text{Fe}^{2+}$  helps melt production. On contrary, Fe metal increases the solidus

temperature. Iron oxide is produced in almost all the samples with Fe metal. This can be explained by a redox reaction between iron and carbon. At 1100 °C, the following reaction occurs  $\text{cpx}_1 + \text{ol}_1 + \text{melt} + \text{Fe} \rightarrow \text{cpx}_2 + \text{ol}_2 + \text{cc} + \text{Fe-ox} + \text{C}$  (1).  $\text{Fe}^{2+/3+}$  is partitioned between all the phases except Fe and C. At and above 1200 °C, iron metal makes cpx disappear. The redox reaction can be written  $\text{cpx} + \text{ol}_1 + \text{Fe} + \text{melt}_1 \rightarrow \text{ol}_2 + \text{Fe-ox} + \text{melt}_2 + \text{C}$  (2), with  $\text{melt}_2$  containing less carbon than  $\text{melt}_1$ . The presence of a graphite capsule increases the liquidus temperature in the DS series of experiments and reduces the melt content in the DM series.

**Implications for Martian mantle melting.** We can deduce from our 1100 °C experiments that an  $\text{Fe}^0$ -bearing Martian mantle would allow the stability of carbonate at shallower depths than the Earth's. On contrary, an  $\text{FeO}$ -bearing mantle may produce melting. Although our starting compositions contain less  $\text{SiO}_2$  and more  $\text{CO}_2$  than the proposed nakhlite parent magmas [18], the recovered olivines and clinopyroxenes are very similar to those found in nakhlites. This is concordant with the hypothesis that melting of carbonate-silicate portions of the Martian mantle may either participate in the generation of nakhlite parent magmas, or produce liquids that metasomatised the nakhlite source region.

**References:** [1] Zhang R.Y. and Liou J.G. (1994) *Amer. Min.* 79, 397-400. [2] Martin A.M. (2009) *PhD thesis*, Universite Blaise Pascal, Clermont-Ferrand [3] Deines P. (2002) *Earth-Science Reviews* 58, 247-278 [4] Righter K., et al. (2008) *Meteoritics and Planet. Sci.* 43, 10, 1709-1723 [5] Hirschmann M.M. and Withers A.C. (2008) *Earth and Planet. Sci. Lett.* 270, 147-155 [6] Longhi J. (1989) *Proc. of the 19th LPSC*, 451-464 [7] Dreibus and Wänke (1985) *Meteoritics* 20, 367-382 [8] Bertka C.M. and Fei Y. (1996) *Planetary and Space Science* 44, 11, 1269-1276 [9] Takahashi E. (1986) *Journal of Geophysical Res.-Solid Earth and Planets* 91, B9, 9367-9382 [10] Médard E. et al. (2008) *Amer. Min.* 93, 1838-1844 [11] Hammouda T. (2003) *Earth Planet. Sci. Lett.* 214, 357-368 [12] Yaxley G.M. and Brey G.P. (2003) *Contrib. Mineral. Petrol.* 146, 606-619 [13] Dasgupta R. et al. (2004) *Earth Planet. Sci. Lett.* 227, 73-85 [14] Dasgupta R. and Hirschmann M.M. (2007) *Amer. Mineral.* 92, 370-379 [15] Brey G.P., et al. (2008) *Journal of Petrol.* 49, 4, 797-821 [16] Goldsmith J.R. et al. (1962) *Journal of Geol.* 70, 659-687 [17] Toplis M.J. and Carroll M.R. (1995) *Journal of Petrology* 36, 5, 1137-1170 [18] Treiman A.H. (2005) *Chem. Der Erde* 65, 203-270.